

# Supporting Information for "Gas-Phase Cytosine and Cytosine-N<sub>1</sub>-Derivatives Have 0.1 - 1 Nanosecond Lifetimes Near the $S_1$ State Minimum"

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## Lifetime fits

The  $S_1$  ( $^1\pi\pi^*$ ) state population is fitted to the following model

$$\frac{d[S_1]}{dt} = -(k_{IC,v}^{S_1} + k_{ISC,v}^{S_1} + k_{rad}^{S_1}) \cdot [S_1] \quad (1)$$

where the first term is the  $S_1 \rightarrow S_0$  radiative decay rate  $k_{rad}$ . The SCS-CC2/aug-cpVDZ calculated radiative lifetimes  $\tau_{rad} = k_{rad}^{-1}$  of cytosine, N<sub>1</sub>-methylcytosine, N<sub>1</sub>-ethylcytosine and N<sub>1</sub>-isopropylcytosine are given in Table S1. The  $S_1$  state is assumed to decay nonradiatively to  $S_0$  by internal conversion (IC) with the rate  $k_{IC}^{S_1}$  and in parallel to the triplet  $T_1$  state with the intersystem crossing (ISC) rate constant  $k_{ISC}^{S_1}$ . Since the lowest  $^1n\pi^*$  state is calculated to lie above the lowest  $^1\pi\pi^*$  state with the SCS-CC2 method, we do not consider it in the relaxation pathway model.

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However, should the  $^1n\pi^*$  lie below the  $^1\pi\pi^*$  state, e.g., for N<sub>1</sub>-isopropylcytosine, the transients do not exclude a relaxation mechanism  $^1\pi\pi^* \rightsquigarrow ^1n\pi^* \rightsquigarrow S_0$ , in which the  $^1n\pi^* \rightsquigarrow S_0$  relaxation is much faster than the  $^1\pi\pi^* \rightsquigarrow ^1n\pi^*$  rate. In this case, the  $k_{IC}^{S_1}$  rate constant would characterize the  $^1\pi\pi^* \rightsquigarrow ^1n\pi^*$  internal conversion.

The lifetimes indicated in Fig. 2, Figures S1 to S3 and given in Table S1 are  $\tau = (k_{IC}^{S_1} + k_{rad}^{S_1} + k_{ISC}^{S_1})^{-1}$ , corresponding to the exponential decay of the  $S_1$  state in eqn.(1). The  $T_1$  state is populated with the rate  $k_{ISC}^{S_1}$  and relaxes to  $S_0$  by  $T_1 \rightsquigarrow S_0$  ISC as well as by phosphorescence; these pathways are combined into one constant  $k_T = k_{ISC}^{T_1} + k_{phos}$ :

$$\frac{d[T_1]}{dt} = k_{ISC}^{S_1} \cdot [S_1] - k_T \cdot [T_1] \quad (2)$$

The ns excitation/ionization transients (for cytosine, see ref. 1) show that the  $T_1$  decay is on the  $\sim 200$  ns timescale, so  $k_T$  is small compared to the other rates and is set to zero for the fits. Using the calculated  $k_{rad}$ , the rate constants  $k_{ISC}^{S_1}$  and  $k_{IC}^{S_1}$  are least-squares fitted to the observed transients.

The ps pump/ionization transients were fitted using a program written in IDL, which employs a Levenberg-Marquardt nonlinear least-squares fit of the transient ion signal to eqns.(1) and (2). This decay model is then convoluted with the instrument response function (IRF), which accounts for the convolution of the pulse widths of the pump and ionisation lasers. The IRF was determined from the rise of the decay curve and can be represented by a Gaussian with a full width at half-maximum (FWHM) of 20 ps.

We note that the fitted values of  $k_{IC}$  and  $k_{ISC}$  are based on the assumption that the ionization cross sections ( $\sigma_{ion}(S_1), \sigma_{ion}(T_1)$ ) for the  $S_1$  and triplet states are equal. For cytosine, the ratio of cross-sections has been estimated to be  $\sigma_{ion}(S_1)/\sigma_{ion}(T_1) \sim 3$  at the ionization wavelength of 215 nm.<sup>1</sup> For the N<sub>1</sub>-substituted cytosines the ratio has not yet been calculated, we estimate it to be between  $\sigma_{ion}(S_1)/\sigma_{ion}(T_1) \sim 1 - 2$ . Thus the  $k_{IC}$  and  $k_{ISC}$  values given in Table S1 must be only considered as indicative, and an improved treatment might increase the  $k_{ISC}$  by up to 3x.

**Table S1:** Excited state lifetimes  $\tau$  of  $S_1$  state keto-amino cytosine,  $N_1$ -methylcytosine,  $N_1$ -ethylcytosine and  $N_1$ -isopropylcytosine, as a function of vibrational level  $v$ , calculated radiative lifetimes and selected  $k_{IC}$  and  $k_{ISC}$  values.

	Transition <sup>a</sup>	Exp. lifetime $\tau$ <sup>b</sup> $S_1$ / ps	$\tau_{rad}$ <sup>c</sup> $S_1 \rightarrow S_0$ / ns	$k_{IC,v}^{S_1}$ <sup>d</sup> $s^{-1}$	$k_{ISC,v}^{S_1}$ <sup>e</sup> $s^{-1}$
Cytosine	$0_0^0$	$730 \pm 60$	18.7	$1.2 \cdot 10^9$	$1.0 \cdot 10^8$
	$0_0^0 + 92$	$460 \pm 50$			
$N_1$ -Methylcytosine	$0_0^0 + 66$	$600 \pm 290$	12.5	$1.2 \cdot 10^9$	$4 \cdot 10^8$
	+201	$230 \pm 70$			
	+274	$96 \pm 10$			
	+297	$106 \pm 60$			
	+339	$100 \pm 15$			
	+372	$50 \pm 15$			
	+401	$13 \pm 8$			
	+429	$20 \pm 4$			
	+460	$20 \pm 2$			
	+516	$< 20$			
$N_1$ -Ethylcytosine	$0_0^0$	$930 \pm 60$	11.8	$7.9 \cdot 10^8$	$2 \cdot 10^8$
	$0_0^0 + 53$	$930 \pm 60$			
	+104	$1030 \pm 270$			
	+153	$630 \pm 70$			
	+240	$350 \pm 60$			
	+317	$280 \pm 20$			
	+444	$88 \pm 5$			
	+519	$27 \pm 2$			
	+571	$25 \pm 3$			
	+613	$22 \pm 2$			
$N_1$ -Isopropylcytosine	$0_0^0 + 40$	$100 \pm 60$	10.9	$9.5 \cdot 10^9$	$3.9 \cdot 10^8$
	+111	$90 \pm 10$			
	+152	$105 \pm 10$			
	+193	$90 \pm 10$			
	+234	$100 \pm 5$			
	+306	$40 \pm 3$			
	+347	$28 \pm 4$			

<sup>a</sup> In  $cm^{-1}$  relative to the respective  $0_0^0$  band ( $31835\text{ cm}^{-1}$  for Cyt,  $31852\text{ cm}^{-1}$  for  $N_1$ -methyl-Cyt,  $31906\text{ cm}^{-1}$  for  $N_1$ -ethyl-Cyt,  $31786\text{ cm}^{-1}$  for  $N_1$ -isopropyl-Cyt)

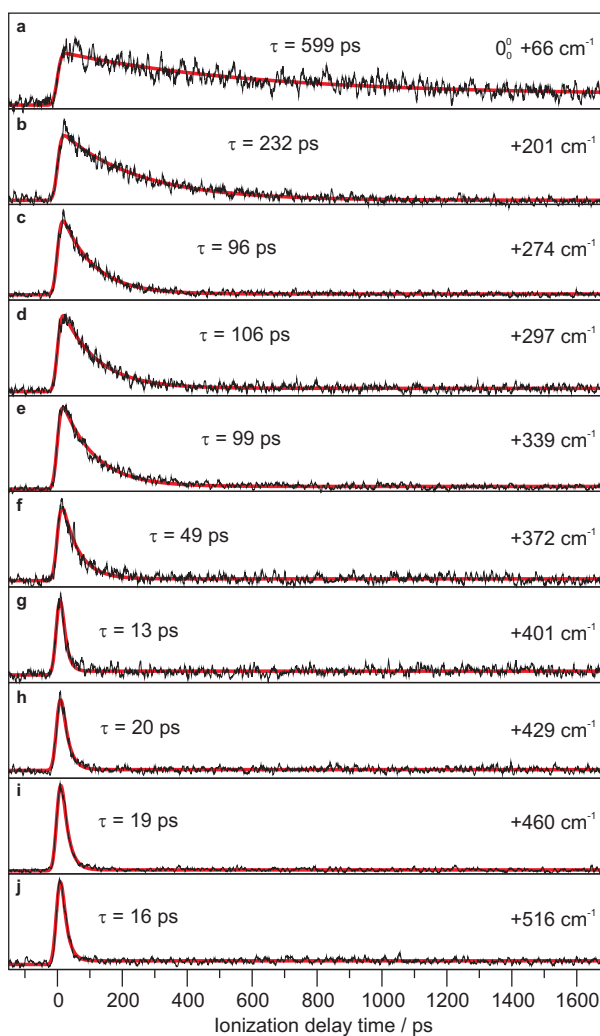
<sup>b</sup> Uncertainties  $\pm 1\sigma$ ; from fitting four to eight separate transients.

<sup>c</sup> Radiative lifetime, calculated at the SCS-CC2/aug-cc-pVDZ level.

<sup>d</sup> Internal conversion rate constant, uncorrected for relative ionization cross sections, estimated error  $\pm 50\%$ .

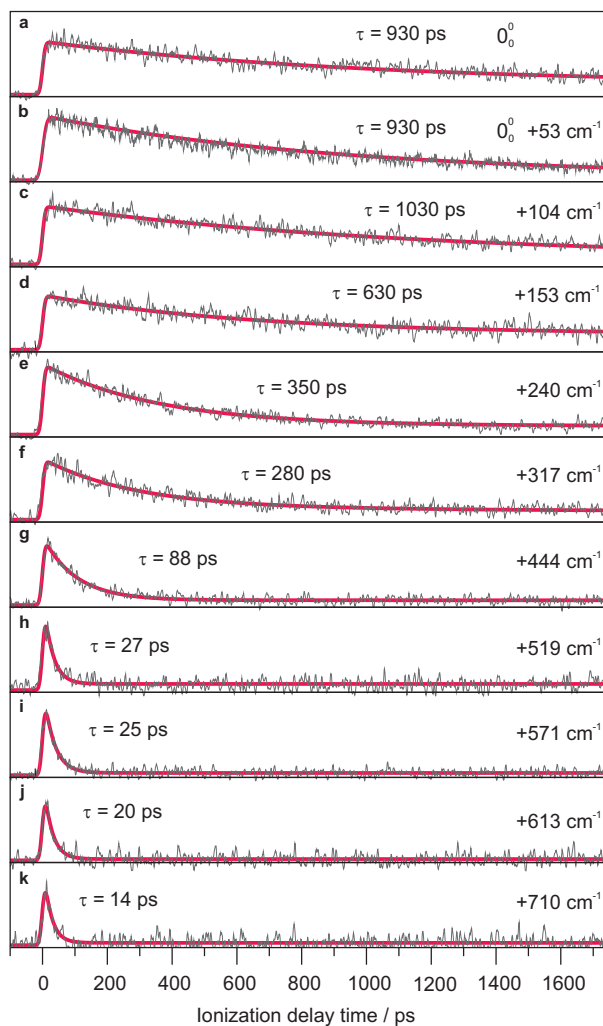
<sup>e</sup> Intersystem crossing rate constant, uncorrected for relative ionization cross sections, estimated error  $\pm 100\%$ .

# N1-Methylcytosine Excited State Lifetimes



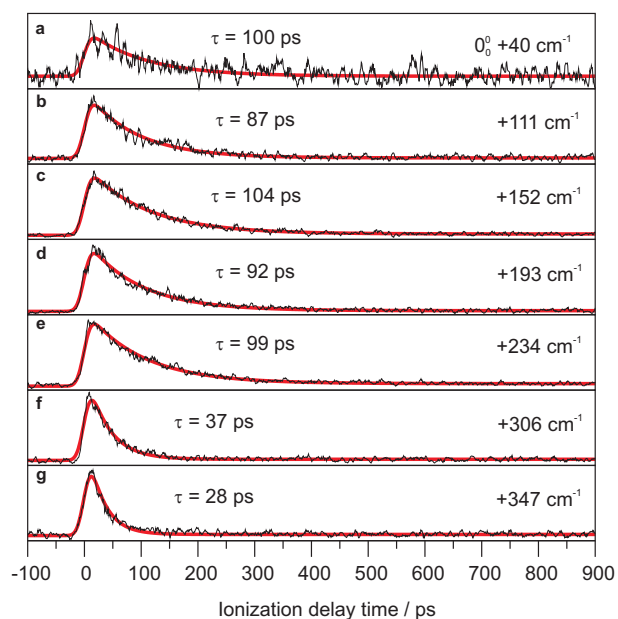
**Fig. S1:** Picosecond pump/delayed ionisation transients of 1-methylcytosine, as a function of vibrational excess energy from the  $0_0^0 + 66 \text{ cm}^{-1}$  level up to  $0_0^0 + 516 \text{ cm}^{-1}$ . The decay times are dominated by  $S_1 \leadsto S_0$  internal conversion. The transients in (a), (b) and (g) exhibit minor growth contributions from  $S_1 \leadsto T_1$  intersystem crossing.

# N1-Ethylcytosine Excited State Lifetimes



**Fig. S2:** Picosecond pump/delayed ionisation transients of 1-ethylcytosine, as a function of vibrational excess energy from the  $v' = 0$  level up to  $0_0^0 + 710 \text{ cm}^{-1}$ . The decay times  $\tau$  are dominated by  $S_1 \rightsquigarrow S_0$  internal conversion. The transients in (a), (d-h) show minor growth from  $S_1 \rightsquigarrow T_1$  intersystem crossing

# N1-Isopropylcytosine Excited State Lifetimes



**Fig. S3:** Picosecond pump/delayed ionisation transients of 1-isopropylcytosine as a function of vibrational excess energy. Most transients are dominated by  $S_1 \leadsto S_0$  internal conversion. The transient in (a) exhibits a small contribution from  $S_1 \leadsto T_1$  intersystem crossing, see Table S1.

**Table S2:** SCS-CC2/aug-cc-pVDZ calculated Cartesian coordinates (in Å) of the  $S_0$  and lowest excited  $^1\pi\pi^*$  minima of amino-keto cytosine, N<sub>1</sub>-methylcytosine and N<sub>1</sub>-ethylcytosine, and the  $^1n\pi^*$  state N<sub>1</sub>-ethylcytosine.

$S_0$ state				$^1\pi\pi^*$ state				$^1n\pi^*$ state <sup>a</sup>			
Cytosine											
C	1.510755	0.009395	2.297425	C	1.488479	0.056142	2.179954				
N	2.654382	0.010716	1.443467	N	2.645117	-0.206218	1.464894				
C	2.580728	-0.000892	0.07691	C	2.63231	0.037881	0.067744				
C	1.352846	-0.015555	-0.537288	C	1.339701	0.043873	-0.530404				
C	0.20272	-0.013546	0.344567	C	0.208974	-0.032824	0.270747				
N	0.268585	0.003596	1.674683	N	0.296739	0.183529	1.697703				
N	-1.055394	-0.079229	-0.211137	N	-1.110484	-0.248028	-0.165473				
O	1.685213	0.020015	3.521133	O	1.727133	0.194223	3.513583				
H	3.550942	0.020198	1.921403	H	3.505724	-0.335002	1.989481				
H	3.527418	-0.000524	-0.469646	H	3.579301	0.226812	-0.438002				
H	1.259478	-0.038235	-1.624318	H	1.258689	0.102594	-1.621988				
H	-1.825888	0.100455	0.425113	H	-1.784945	0.251881	0.413964				
H	-1.178745	0.203693	-1.175726	H	-1.253696	-0.054777	-1.155616				
N <sub>1</sub> -Methylcytosine											
N	-0.012088	-0.023294	-0.027735	N	-0.026775	0.092043	-0.004685				
C	0.00234	-0.013333	1.358961	C	0.077904	0.044842	1.29032				
N	1.280412	-0.00313	2.011758	N	1.253149	-0.061763	2.023967				
C	2.447181	-0.010384	1.299909	C	2.453658	0.254642	1.339347				
C	2.437831	-0.02979	-0.076054	C	2.42045	0.153265	-0.083539				
C	1.137239	-0.037038	-0.700071	C	1.210392	-0.065115	-0.720624				
O	-1.014596	-0.005548	2.066717	O	-1.04709	0.088593	2.043108				
N	1.051159	-0.11186	-2.075892	N	1.024714	-0.387692	-2.076767				
C	1.268955	0.016087	3.482186	C	1.265963	-0.155915	3.48659				
H	3.373322	-0.003159	1.881759	H	3.313701	0.561082	1.937101				
H	3.367394	-0.050781	-0.647709	H	3.355345	0.251062	-0.647959				
H	0.130922	0.081233	-2.459891	H	0.158618	0.009304	-2.441084				
H	1.843253	0.205464	-2.622514	H	1.820525	-0.152388	-2.667997				
H	2.309985	0.019909	3.837452	H	2.122949	-0.784137	3.775977				
H	0.740902	0.913406	3.836856	H	1.373234	0.843142	3.946295				
H	0.739571	-0.871007	3.859681	H	0.327046	-0.614189	3.825363				
N <sub>1</sub> -Ethylcytosine											
C	1.132861	0.002326	-0.736622	C	1.213014	-0.027455	-0.788083	N	0.430142	-0.11916	0.785762
N	0.089871	0.634064	-0.201917	N	-0.013502	0.460879	-0.21386	C	1.574837	0.122921	-0.040926
C	0.027875	0.826575	1.170428	C	0.024198	0.665668	1.072781	C	1.336462	0.193606	-1.447659
N	1.141538	0.372233	1.955331	N	1.088153	0.367905	1.927522	C	0.062655	0.023774	-1.952676
C	2.198528	-0.279191	1.382951	C	2.052247	-0.54284	1.431982	N	-1.081171	-0.026374	-1.084620
C	2.250955	-0.497411	0.025395	C	2.160699	-0.647118	0.014684	C	-0.789188	-0.133418	.170554
O	-0.921735	1.373765	1.749313	O	-1.031438	1.229401	1.689106	N	-0.279099	-0.135236	-3.309091
C	1.061266	0.54187	3.420589	C	1.022489	0.645183	3.372104	O	-1.856966	-0.294407	1.043661
N	1.094544	-0.216704	-2.099358	N	1.189001	-0.066298	-2.197324	C	0.593486	-0.518360	2.195853
H	2.989793	-0.608764	2.063155	H	2.723028	-1.012881	2.15209	C	0.171858	0.577798	3.183373
H	3.092136	-1.020724	-0.432874	H	2.979776	-1.232907	-0.418011	H	2.461106	0.525074	0.457132
H	0.393384	0.320491	-2.600802	H	0.54067	0.624924	-2.572381	H	2.190786	0.351391	-2.116138
H	1.971226	-0.37488	-2.582484	H	2.108246	0.026053	-2.625377	H	-1.206584	0.239976	-3.506372
C	0.208717	-0.555094	4.068534	C	0.338973	-0.482021	4.160443	H	0.416530	0.240227	-3.951893
H	2.095186	0.525217	3.803881	H	2.065797	0.781643	3.703768	H	1.658661	-0.770496	2.312595
H	0.6258	1.533986	3.606448	H	0.479889	1.593897	3.499577	H	-0.000584	-1.434774	2.360982
H	0.159791	-0.396937	5.159395	H	0.35485	-0.246394	5.238193	H	0.366971	0.242252	4.216455
H	-0.813376	-0.524724	3.661498	H	-0.710338	-0.59026	3.840026	H	0.741924	1.503906	3.001914
H	0.644887	-1.55086	3.879374	H	0.857497	-1.442143	4.005000	H	-0.903412	0.801389	3.091703

<sup>a</sup> Upon rotation of the ethyl group in the  $S_1$  state of N<sub>1</sub>-ethylcytosine towards the molecular plane and the keto oxygen, the  $S_1$  state character changes from pure  $^1\pi\pi^*$  to nearly pure  $^1n_O\pi^*$ . The geometry given corresponds to the lowest energy beyond which the  $^1n_O\pi^*$  character is dominant (> 59% contribution to the  $S_1$  state). However, this is not a stationary point.

**Table S3:** SCS-CC2/aug-cc-pVDZ calculated Cartesian coordinates (in Å) of the  $S_0$  state and lowest excited  $^1\pi\pi^*$  and  $^1n\pi^*$  state minima of keto-amino  $N_1$ -isopropylcytosine.

	$S_0$ state				$^1\pi\pi^*$ state				$^1n\pi^*$ state		
C	1.100371	0.034632	-0.73331	C	1.134566	0.039650	-0.747939	C	1.504169	0.06581	-1.383724
N	0.0128	0.38967	-0.052906	N	0.426748	1.042771	-0.001775	C	0.354151	0.007734	-2.146683
C	0.017787	0.342489	1.333252	C	0.473282	0.905712	1.295489	N	-0.937508	-0.051253	-1.532691
N	1.258768	0.01319	1.986337	N	1.223330	-0.046331	1.995291	C	-0.912849	0.014733	-0.248218
C	2.35161	-0.373808	1.261318	C	2.280653	-0.653374	1.276645	N	0.125725	0.166409	0.62127
C	2.331638	-0.386485	-0.115089	C	2.152270	-0.683228	-0.145757	C	1.44106	0.053583	0.040204
O	-0.979207	0.582667	2.029631	O	-0.243915	1.730296	2.073120	N	0.300076	-0.145164	-3.548224
C	1.242337	-0.047441	3.474336	C	1.112266	-0.209415	3.463811	O	-2.185652	-0.053014	0.356172
N	0.99914	0.032124	-2.110858	N	0.728562	-0.042708	-2.092286	C	-0.094048	-0.125345	2.059293
H	3.239645	-0.664559	1.826209	H	3.127656	-1.054142	1.834395	C	0.029629	-1.634127	2.327972
H	3.20477	-0.700413	-0.690159	H	2.865377	-1.272927	-0.734919	C	0.854788	0.706962	2.932148
H	0.187201	0.517519	-2.480974	H	0.414840	0.862304	-2.443614	H	2.271037	0.370315	0.673256
H	1.853262	0.109554	-2.650912	H	1.427247	-0.45841	-2.706790	H	2.49008	0.085285	-1.861667
C	2.596286	0.345279	4.081004	C	2.202345	0.597882	4.189193	H	-0.559298	0.248717	-3.930497
H	0.485347	0.695948	3.763975	H	0.127147	0.209091	3.722964	H	1.116528	0.234083	-4.025299
C	0.775811	-1.438542	3.926962	C	1.144182	-1.701245	3.831126	H	-1.128383	0.203556	2.274929
H	2.464898	0.482216	5.167132	H	2.079782	0.493481	5.280802	H	0.55236	0.605003	3.987761
H	3.363743	-0.435191	3.940706	H	3.208374	0.235244	3.918307	H	1.895148	0.354177	2.845106
H	2.965276	1.29343	3.655617	H	2.129016	1.666446	3.928205	H	0.810589	1.772361	2.65423
H	0.695432	-1.472645	5.027122	H	0.904814	-1.810593	4.902527	H	-0.170994	-1.847211	3.391943
H	-0.211082	-1.66688	3.495453	H	0.398514	-2.262027	3.244649	H	-0.692193	-2.200211	1.715472
H	1.498948	-2.209643	3.60577	H	2.137725	-2.145369	3.657171	H	1.047066	-1.977133	2.079129



**Table S4:** SCS-CC2/aug-cc-pVDZ adiabatic and vertical  $^1\pi\pi^*$  and  $^1n\pi^*$  energies.

	$^1\pi\pi^*$ state	$^1n\pi^*$ state	
	adiabatic	adiabatic	vertical
Cytosine	31857		34487
N <sub>1</sub> -Methylcytosine	31899		34724
N <sub>1</sub> -Ethylcytosine	31966	32372 <sup>a</sup>	34893
N <sub>1</sub> -Isopropylcytosine	31701	31868	35051

<sup>a</sup> Not a minimum structure, see footnote in Table S3.

## References

- (1) Lobsiger, S.; Etinski, M.; Blaser, S.; Frey, H.-M.; Marian, C.; Leutwyler, S. Intersystem Crossing Rates of  $S_1$  State Keto-Amino Cytosine at Low Excess Energy. *J. Chem. Phys.* **2015**, *143*, 234301–1–12.